

Effect of boron additive on the cycle life of low-Co AB₅-type electrode consisting of alloy prepared by cast and rapid quenching

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Received 25 June 2003; received in revised form 30 July 2003; accepted 6 August 2003

Abstract

In order to modify the cycle stability of low-Co AB₅-type alloy, a trace of boron was added in MmNi_{3.8}Co_{0.4}Mn_{0.6}Al_{0.2} hydrogen storage alloy. The low-Co AB₅-type alloys MmNi_{3.8}Co_{0.4}Mn_{0.6}Al_{0.2}B_x ($x = 0, 0.1, 0.2, 0.3, 0.4$) were prepared by cast and rapid quenching. The cycle lives and microstructures of the as-cast and quenched alloys were measured and analyzed. The effects of boron additive on the microstructures and cycle lives of as-cast and quenched alloys were investigated comprehensively. The obtained results showed that the addition of boron could dramatically enhance the cycle lives of the as-cast and quenched alloys. When boron content x increases from 0 to 0.4, the cycle lives of the as-cast alloys were increased from 118 to 183 cycles, and for as-quenched alloys with quenching rate of 38 m/s from 310 to 566 cycles.

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Keywords: Low-Co AB₅-type alloy; Boron additive; Cast and rapidly quenched; Cycle life

1. Introduction

AB₅-type (original LaNi₅) rare-earth-based hydrogen storage alloy, which can reversibly absorb and desorb hydrogen at room temperature and can be easily activated as well as produce high reacting rate of absorbing and desorbing hydrogen, is being used widely. Although AB₅-type hydrogen storage alloy has realized large-scale industrialization in many countries, especially in Japan and China, the investigation on the AB₅-type rare-earth-based hydrogen storage alloy has been carrying out in order to improve the electrochemical characteristics and reduce the production cost of the alloy [1,2]. The majority of the papers published by International Symposium on Metal Hydrogen System-Fundamental and Applications, Anney, France, September 2002 still concentrated on the investigation of AB₅-type hydrogen storage alloy.

The decrease of Co content in alloy is very beneficial to reduce the production cost of the alloy, whereas the effect of Co on the cycle life of the AB₅-type hydrogen storage

alloy is extremely important [3]. Therefore, the investigation focus on AB₅-type hydrogen storage alloy is how to enhance the cycle stability of low-Co electrode alloy. The AB₅-type hydrogen storage alloy with special microstructure, which is composed of microcrystal and nanocrystal as well as amorphous phase, can be prepared by composition adjusting and rapid quenching [4]. The alloy thus prepared has excellent activation performance and cycle stability. In order to enhance the cycle stability of low-Co AB₅-type alloy, a trace of boron was added in MmNi_{3.8}Co_{0.4}Mn_{0.6}Al_{0.2} hydrogen storage alloy, and rapid quenching technique was used in the preparation of the alloys. The obtained results indicated the cycle lives of the as-cast and quenched alloys could be enhanced dramatically, whereas the effect mechanics of boron on the cycle lives of the as-cast and quenched alloys are completely different.

2. Experimental details

2.1. Preparation of alloys

The chemical composition of the experimental alloy was MmNi_{3.8}Co_{0.4}Mn_{0.6}Al_{0.2}B_x ($x = 0, 0.1, 0.2, 0.3, 0.4$). Corresponding with boron content x , the alloys were represented

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with B₀, B₁, B₂, B₃, B₄. The purity of all the component metals (Ni, Co, Mn, Al) is at least 99.8 wt.%. The purity of boron is 99.93 wt.%. Mm denotes Ce-rich Mischmetal (23.70 wt.% La, 55.29 wt.% Ce, 5.28 wt.% Pu, 15.70 wt.% Nd). The alloys were melted and cast in an argon atmosphere using an induction furnace. Part of the as-cast alloys was re-melted and quenched by melt-spinning with a rotating copper wheel, obtaining flakers of as-quenched alloy with quenching rate of 22, 30, and 38 m/s. The quenching rate was expressed by the linear velocity of the copper wheel.

2.2. Electrode preparation and electrochemical measurement

The fractions of the as-cast and quenched alloys, which were ground mechanically into powder below 200 meshes, were used for the preparation of the experimental electrode. The electrode pellets with 15 mm in diameter were prepared by mixing 1 g alloy powder and 1 g Ni powder as well as a trace of polyvinyl alcohol (PVA), and then compressed under a pressure of 35 MPa. After drying for 4 h, the electrode pellets were immersed in 6 M KOH solution for 24 h.

The experimental electrodes were tested in a tri-electrode open cell, which consists of a working electrode (metal hydride electrode), a counter electrode (NiOOH/Ni(OH)₂) and a reference electrode (Hg/HgO). The electrolyte was a 6 M KOH solution. The voltage between the negative electrode and the reference electrode was defined as the discharge voltage. Every cycle was overcharge to about 50% with constant current, resting 15 min and -0.500 V cut-off voltage. The cycle life was measured through constant charge–discharge current density of 300 mA/g. The environment temperature of measurement was kept at 30 °C.

2.3. Microstructure determination and morphology observation

The samples of the as-cast alloys were directly polished, and pieces of flake of the as-quenched alloys were inlaid in epoxy resin for polishing. The samples thus prepared were etched with a 60% HF solution. The morphologies of the as-cast and quenched alloys were observed by SEM and optical microscope. The samples of the as-cast and quenched alloys were pulverized by mechanical grinding, and the size of the powder sample was <75 μm . The phase structures of the alloys were detected by XRD, and the type of X-ray diffractometer used in this experiment was D/max/2400. The diffraction was performed with Cu K α 1 and the rays were filtered by graphite. The experimental parameters for determining the phase structure were: 160 mA, 40 kV and 10°/min. The lattice constants were measured by step scanning, and the experimental parameters were: 160 mA, 50 kV, 0.02° per step, and 1 s per step equivalent to 1.2°/min. The powder samples were dispersed in absolute alcohol for observing grain morphology with TEM, and for determining with selected area electron diffraction (SAED) whether an amorphous phase existed in the samples.

3. Results and discussion

3.1. The effects of boron on the cycle life

Cycle life indicated by N was characterized by the cycle number after which the discharge capacity of the alloy with the current density of 300 mA/g was reduced to 60% of the maximum capacity. Fig. 1 illustrated the cycle number dependence of the discharge capacity of the alloys prepared by cast and rapidly quenched (22 m/s), respectively,

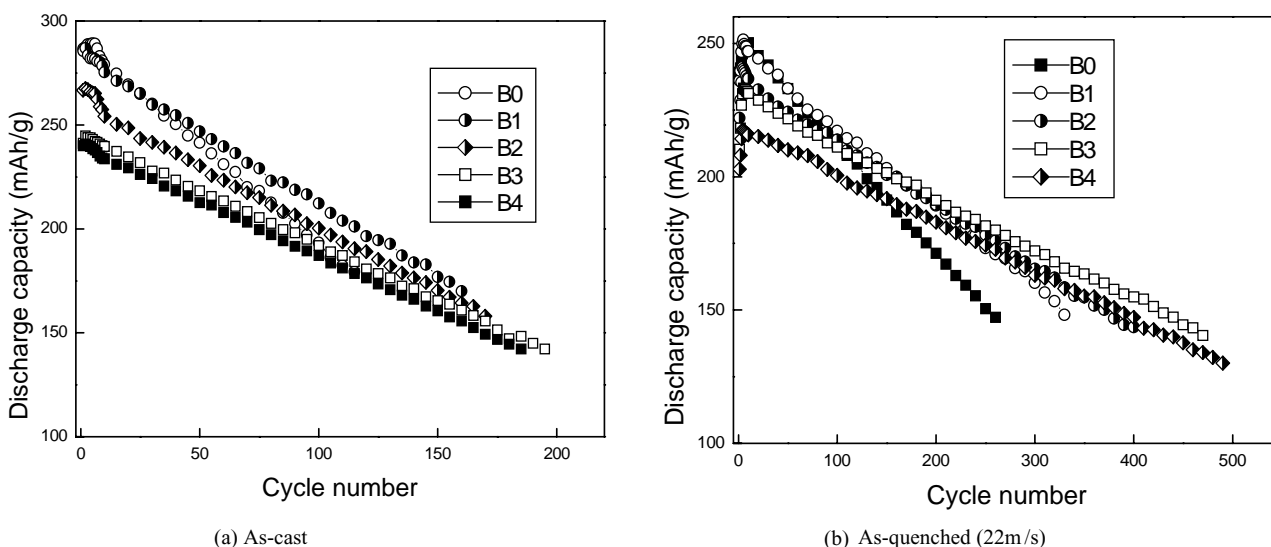


Fig. 1. The relationship between the cycle number and the discharge capacity of the as-cast and quenched alloys.

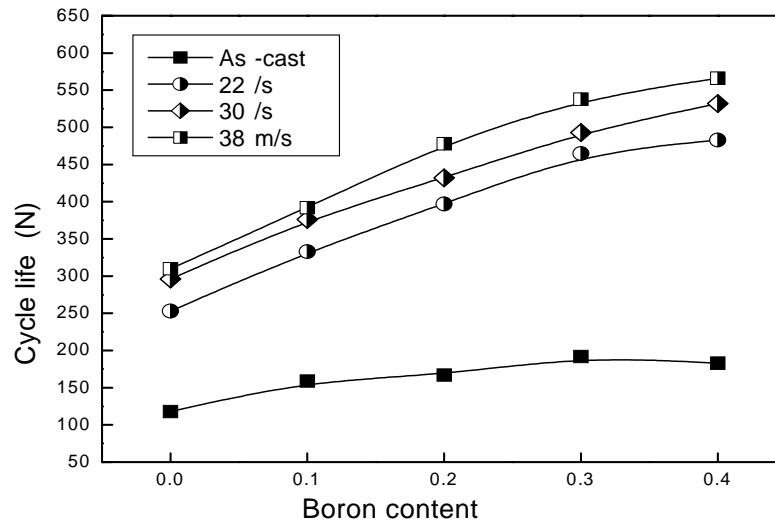


Fig. 2. The relationship between the boron content and the cycle life of the as-cast and quenched alloys.

and charge–discharge current density is 300 mA/g. It can be derived from Fig. 1 that the inclination slopes of the curves corresponding with as-cast and quenched alloys decrease with the increase of boron content x . It indicated that the addition of boron is favourable to the cycle lives of the alloys. In order to show clearly the effect of boron on the cycle lives of the alloys, the boron content x dependence of the cycle lives of the as-cast and quenched alloys was illustrated in Fig. 2. It can be seen from Fig. 2 that the cycle lives of the as-cast and quenched alloys significantly increase with the increase of boron content x . When boron content x increases from 0 to 0.4, the cycle life of the as-cast alloy was enhanced from 118 to 183 cycles, and for as-quenched alloys from 310 to 566 cycles. Obviously, the effect of boron on the cycle life of the as-quenched alloy is more significant than on that of the as-cast alloy. Fig. 3 illustrate the cycle

number dependence of the discharge capacity of the as-cast and quenched B_4 alloy, and the charge–discharge current density is 300 mA/g. It can be derived from Fig. 3 that all of the cycle lives of the as-quenched are longer than that of the as-cast alloy, and the cycle lives of as-quenched alloys significantly increase with the increase of the quenching rate. It indicated the preparation technique is a decisive factor of the cycle life of the alloy.

3.2. The effects of the boron on the microstructure

3.2.1. Analysis of phase structures

The phase structure of the as-cast and quenched alloys were determined by XRD. Fig. 4 illustrated the X-ray diffraction diagrams of the as-cast and quenched alloys. It can be derived from Fig. 4 that as-cast alloy without boron (B_0) has a single phase structure with $CaCu_5$ -type. However, all of the as-cast alloys with boron (B_1 – B_4) have a two-phase structure that is composed of a $CaCu_5$ -type main phase and a small amount of $CeCo_4B$ -type secondary phase. Both main and secondary phase belong to hexagonal system with $P6/mmm$ space group. The abundance of the $CeCo_4B$ -type secondary phase increases with the increase of the boron content x . The all of the as-quenched alloys (B_0 – B_4) obtained with quenching rate of 22 m/s have a single phase structure with $CaCu_5$ -type, and $CeCo_4B$ -type secondary phase disappears completely. The lattice constants of the as-cast and quenched alloys obtained with quenching rate of 22 m/s, which were calculated from the diffraction peaks of (1 0 1), (1 1 0), (2 0 0), (1 1 1) and (0 0 2) crystal planes of the main phase of the alloys by a method of least squares, were listed in Table 1. It can be derived from Table 1 that the addition of boron has a little influence on the lattice constants of the main phase. The c -axis of the main phase of the as-cast alloy slightly increases with the increase of boron content x , whereas a axis of the main phase decreases imperceptibly.

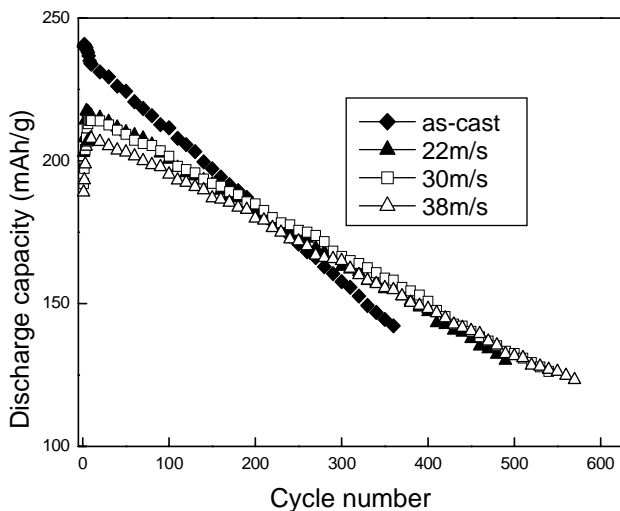


Fig. 3. The relationship between the cycle number and capacity of the as-cast and quenched B_4 alloy.

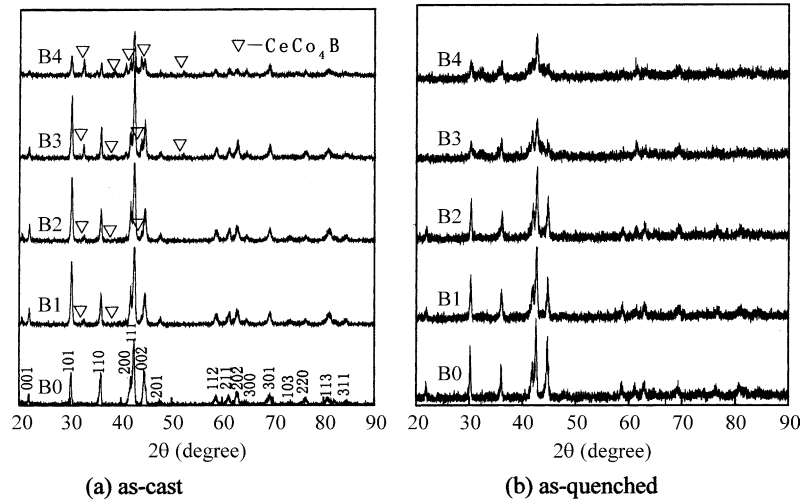


Fig. 4. The X-ray diffraction diagrams of the as-cast and quenched alloys.

It is reasonable to roughly quantify the amount of the secondary phase of the as-cast alloys by using the relative integral intensity of the strongest peak (1 1 1) for CaCu_5 -type phase and the strongest peak (1 1 2) for CeCo_4B -type phase because the main phase and the secondary phase belong to the same space group. The ratio of integral intensity of the peak (1 1 2) for CeCo_4B -type phase versus the total integral intensity of the peak (1 1 1) for CaCu_5 -type phase and the peak (1 1 2) for CeCo_4B -type phase was calculated as the abundance of the secondary phase of the as-cast alloys (B_1 – B_4), and the calculated results were also listed in Table 1. It can be known from Table 1 that the abundance of the secondary phase in the as-cast alloys with boron (B_1 – B_4) increases with the increase of boron content x . When boron content x increases from 0.1 to 0.4, the amount of the secondary phase increase from 3.21 to 20.26%. Further, rapid quenching makes the lattice constants and cell volumes of the alloys increased, and it is favorable for the modification of the cycle stability of the alloys.

The cycle stability of hydrogen storage alloy is a decisive factor of the life of Ni–MH battery. The root cause of leading to battery lose efficacy is on negative electrode, rather than on positive electrode. The failure of battery is characterized by the decay of discharge capacity and the decrease of discharge voltage. The results obtained in the literatures [5,6]

confirmed that the fundamental reason for the capacity decay of the electrode alloy is the pulverization and oxidation of the alloy in process of the charge–discharge cycle. The lattice internal stress and lattice volume expansion, which are inevitable when hydrogen atoms enter into the interstitials of the lattice, are real driving force, which leads to the pulverization of the alloy. The reason for the addition of boron enhancing the cycle life of the as-cast alloy is attributed to the formation of the secondary phase. The formation of the secondary phase increases the amount of phase boundaries, which probably is a buffer area of the releasing of the stress formed in the process of hydrogen absorbing. Therefore, the anti-pulverization property of the as-cast alloy was improved significantly. However, the cycle lives of the alloys with boron were enhanced dramatically by rapid quenching. Obviously, it has no relation with the secondary phase, and the differences of the cycle lives of the alloys with boron (B_1 – B_4) are very large although the same rapid quenching technique was used. So, it is very necessary to further investigate on the microstructure of the alloys in order to explain the mechanism of the change in the cycle life.

3.2.2. Microstructures and morphology

Fig. 5 illustrated the microstructure morphologies of the as-cast and quenched alloys (B_0 and B_4). It can be seen from

Table 1
Cell parameter and volume of CaCu_5 -type main phase; the abundance of secondary phase in the alloys with boron

| Sample | Lattice constant | | | | Cell volume | | Abundance of secondary phase | |
|--------------|------------------|--------|---------|--------|-----------------------|--------|------------------------------|--------|
| | a (Å) | | c (Å) | | V (Å ³) | | Percentage | |
| | As-cast | 22 m/s | As-cast | 22 m/s | As-cast | 22 m/s | As-cast | 22 m/s |
| B_0 | 5.017 | 5.021 | 4.051 | 4.053 | 88.31 | 88.49 | – | – |
| B_1 | 5.016 | 5.023 | 4.053 | 4.054 | 88.32 | 88.58 | 3.21 | – |
| B_2 | 5.016 | 5.022 | 4.059 | 4.062 | 88.45 | 88.72 | 3.88 | – |
| B_3 | 5.015 | 5.024 | 4.061 | 4.062 | 88.45 | 88.78 | 14.48 | – |
| B_4 | 5.014 | 5.023 | 4.061 | 4.063 | 88.42 | 88.78 | 20.26 | – |

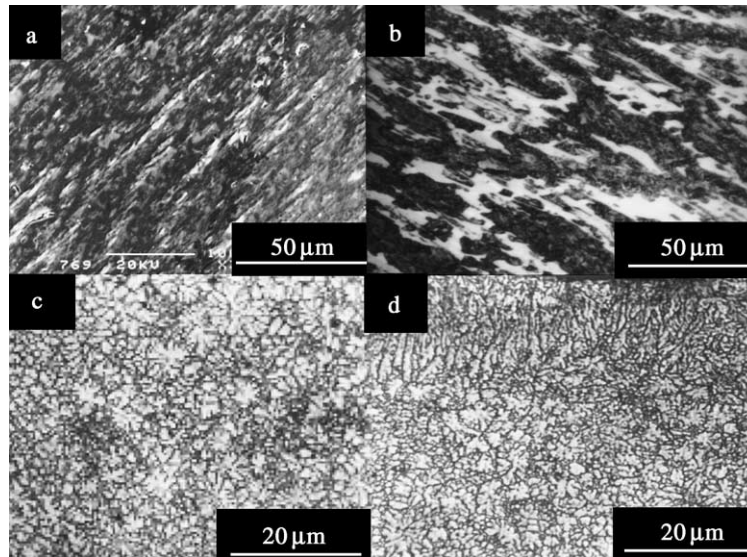


Fig. 5. The morphologies of as-cast and quenched alloys (B_0 and B_4): (a, b) the morphologies of as-cast alloys (B_0 and B_4); (c, d) the morphologies of as-quenched alloys (B_0 and B_4) (22 m/s).

Fig. 5 that rapid quenching lead to the grain sizes of the alloy decreased obviously. Mishima et al. [7] reported that the rapid quenching increases the capacities of $\text{LaNi}_{4.6}\text{Al}_{0.4}$ and $\text{LaNi}_4\text{Co}_{0.6}\text{Al}_{0.4}$ alloys. He considered that the rapid quenching process made the grain of the alloy fine, thus producing an addition amount of grain boundaries that provide good channels for the diffusion of hydrogen atoms. In addition, fine grain can improve the cycle stability of the alloy on a certain degree. Rapid quenching made the grain sizes of the alloys (B_0 and B_4) decreased significantly, whereas the difference of their cycle lives is very large. Obviously, it is not a result to which the difference of the grain sizes of the alloy leads. The microstructures of the alloys were

investigated further so that the mechanism of the cycle lives of the as-quenched alloys (B_0 and B_4) having a large difference can be understood entirely. The crystal state of the alloy was determined by TEM and the obtained results were illustrated in Fig. 6. It can be seen from Fig. 6 that amorphous phase formed in the alloys (B_0 and B_4) obtained with quenching rate of 22 m/s, and the amount of the amorphous phase in B_0 alloy is much less than that in B_4 alloy. A complete crystal morphology of B_0 alloy can be seen clearly, whereas we cannot see a complete crystal morphology in B_4 alloy. It can be seen from Fig. 4b that the X-ray diffraction peak of the B_4 alloy with quenching rate of 22 m/s broaden and the its height lowered significantly. Obviously, it should

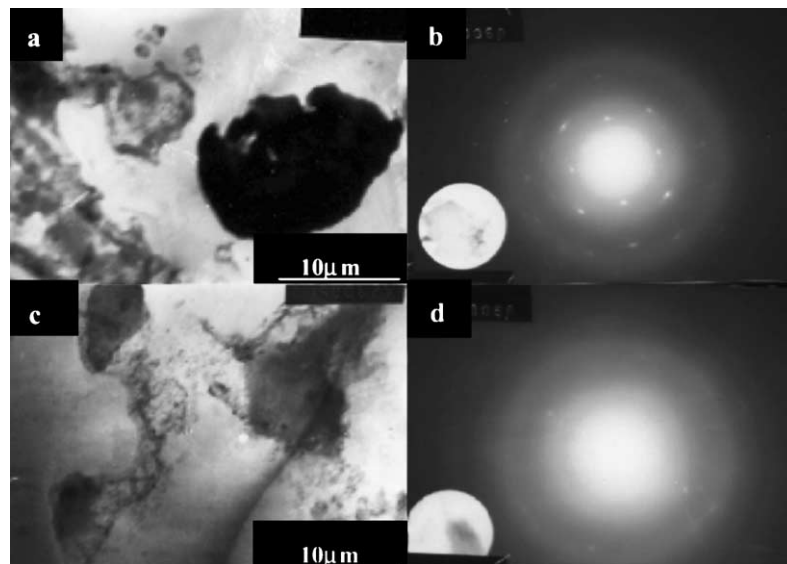


Fig. 6. The morphologies and SAD of the as-quenched alloys (22 m/s) (TEM): (a, c) the morphologies of the as-quenched alloys (B_0 and B_4); (b, d) the diffraction patterns of the as-quenched alloys (B_0 and B_4).

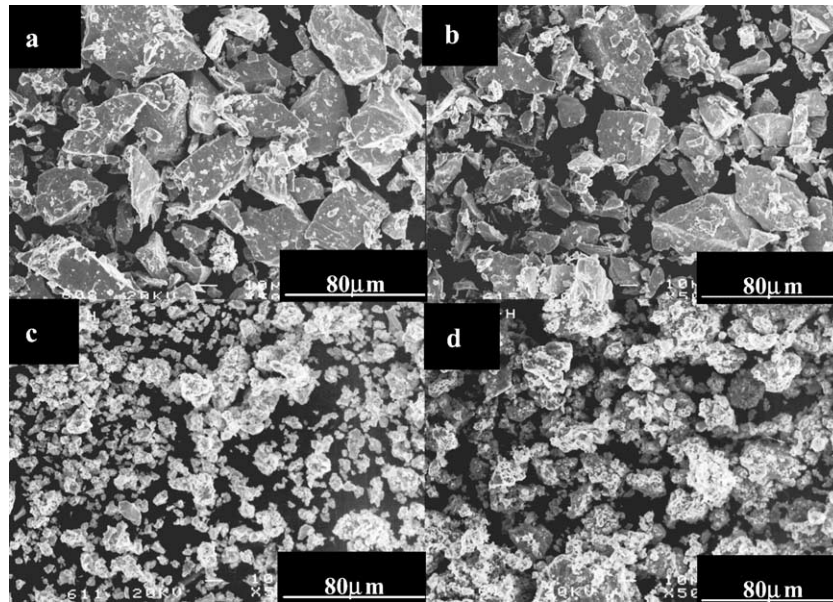


Fig. 7. The granular morphologies of as-quenched alloys (22 m/s) before and after electrochemical cycle (SEM): before cycle (B_0); (b) before cycle (B_4); (c) after cycle (B_0); (d) after cycle (B_4).

be mainly ascribed to the effect of boron. The experimental results indicated that the amount of amorphous phase increases with the increase of quenching rate. Therefore, it can be concluded that the great difference of the cycle lives of the as-quenched alloy with different boron contents was attributed to the difference of the amounts of the amorphous phase in the alloy. The fine grain and amorphous phase are of great particular advantage to the cycle life of the alloy, but the influence of amorphous phase is much stronger. The main reason of boron making the cycle life of the as-quenched alloy dramatically increased is that boron can strongly promote the formation of amorphous phase. Besides composition of the alloy, quenching rate is a predominated factor of the amount of amorphous phase. The higher the quenching rate, the more the amount of amorphous phase and the longer the cycle life of the alloy. The morphologies of as-quenched alloy particles (B_0 and B_4) before and after electrochemical cycle were observed by SEM and the obtained results were illustrated in Fig. 7. It can be seen from Fig. 7 that shapes of B_0 and B_4 alloy particles before electrochemical cycle are irregular, and the sizes of the particles are not uniform. The diameter of the biggest particle is about $70\ \mu\text{m}$, the smallest particle is about $15\ \mu\text{m}$ in diameter. After as-quenched B_0 and B_4 alloys passed 253 and 483 charge–discharge cycles, respectively, both their morphologies had a great change, which displayed the disappearance of the pointedness of the particles and the decrease of the sizes of the particles. It indicated that the main reason of the capacity decay of B_0 and B_4 alloys is the pulverization of the alloys in process of charge–discharge cycle. Worthy of remark is that the cycle number of B_4 alloy is 230 cycles more than that of B_0 alloy, whereas the particle size of B_4 alloy is much larger than that of B_0 alloy. It indicated that the anti-pulverization prop-

erty of B_4 alloy is better. Anti-pulverization performance of alloy depends on the microstructure and phase structure as well as chemical composition of alloy. All of the factors, by which the strength and toughness of the alloy can be modified, significantly enhance the anti-pulverization property of the alloy. Obviously, fine grain is very beneficial to the improvement of the strength and toughness of alloy. The difference of the grain sizes of the as-quenched alloys (B_0 and B_4) is very little (Fig. 5). So B_4 alloy having a stronger anti-pulverization performance is ascribed to B_4 alloy containing a larger amount of amorphous phase. Therefore, it can be concluded that the main reason of boron making the cycle life of the as-quenched alloy dramatically increased is that boron can strongly promote the formation of amorphous phase.

4. Conclusions

- (1) The microstructures of the as-cast alloy $\text{MmNi}_{3.8}\text{Co}_{0.4}\text{Mn}_{0.6}\text{Al}_{0.2}\text{B}_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) are composed of CaCu_5 -type main phase and a small amount of CeCo_4B -type secondary phase, and the abundance of the secondary phase increases with the increase of boron content x . When quenching rate is more than 22 m/s, the secondary phase in the alloys (B_1 – B_4) disappears completely, and all of the as-quenched alloys have a single phase structure.
- (2) The addition of boron significantly enhances the cycle life of the as-cast and quenched alloys. When boron content x increases from 0 to 0.4, the cycle lives of the as-cast alloys were enhanced from 118 to 183 cycles, and for as-quenched alloys obtained with quenching rate of 38 m/s from 310 to 566 cycles.

- (3) The effect mechanisms of boron on the cycle lives of the as-cast and quenched alloys are completely different. Boron increasing the cycle life of the as-cast alloy is attributed to the formation of CeCo₄B-type secondary phase, whereas fundamental reason of boron enhancing the cycle life of the as-quenched alloy is that boron strongly promotes the formation of amorphous phase in the alloy.

Acknowledgements

This work is supported by National Natural Science Foundations of China (50131040 and 50071050).

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